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A MOLECULAR ORBITAL STUDY OF ATMOSPHERICALLY IMPORTANT SPECIES

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RESEARCH OBJECTIVES

Recently balloon-borne mass spectrometers have been utilized to determine the

ionic composition of the earth's ionosphere and stratosphere.[1-7] These studies

indicate that both the positive and negative ions are clustered species. Consequent-

ly, the properties of some of these cluster ions, such as their structures, ener-

getics, and charge distributions, have been under extensive investigation.[8-11]

Information on these properties is needed for the following reasons. First, data

on the structures of these complexes will 1) lead to a more complete understanding

of the forces between ions and neutral molecules, in particular the role of hydrogen

bonding, which is believed to be significant,[10,12,13] in the solvation of positive

and negative ions and 2) provide information on the number of solvent molecules

which can be accomodated by an ion and on its inner and outer solvation shells.

This data is useful since the kinetic properties, electron affinities, mobilities,

and products of the ionic recombination reactions of these clusters are believed to

be dependent on their sizes.[14] Second, thermodynamic data on clustering reactions

is required in the theoretical development of aerosol formation[10] and in the theo-

retical development of the chemical mechanisms involving negative ions which cause

radio and radar blackout, i.e. photodetachment and photodissociation.[14] Third, the

calculated charge distributions will indicate whether the positive or negative

charge is relatively evenly distributed or whether it is localized as is assumed in

some electrostatic models used to compute bond energies.

In particular, cluster ions of NO_3^- with H_2O have received considerable attention

recently.[10,11,15-18] Wu and Tiernan[11] have generated ions of this type from reaction

mixtures containing various combinations of NO, NO_2, H_2O, O_2, and O_3. One type of

product ion they reported has the general formula $OH^- \cdot HNO_3$. Only one ion with this

general formula (bond dissociation energy approximately 75 kcal/mole) was obtained.

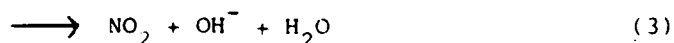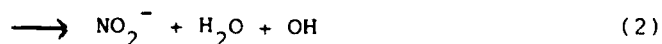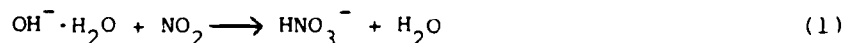These results agree with those of Paulson[16] and Yamdagni and Kebarle.[17]

One objective of this work was to use <u>ab initio</u> molecular orbital (MO) theory to
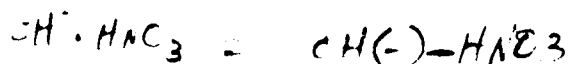
determine the optimum structure of $OH^- \cdot HNO_3^-$ and to compute its adiabatic electron affinity, bond dissociation energy and charge distribution. Thus, a study of $OH^- \cdot HNO_3$ and a series of simpler molecules and ions, which contain similar types of bonds and whose structures and adiabatic electron affinities are known, was carried out to find the most economical basis set which yields reliable results. The other molecules and ions considered were OH, OH^-, NH, NH^-, NH_2, NH_2^-, OOH, OOH^-, NO_2, NO_2^-, H_2O, $OH^- \cdot H_2O$, HNO_3, and HNO_3^-. Basis sets with and without polarization functions, diffuse functions, and configuration interaction were utilized to investigate their effect on the properties of the above species.

A second objective of this work was to probe the accuracy of the various basis sets in calculating energy changes for reactions involving negative ions. The set of reactions chosen for this purpose was the set observed by Paulson and Dale[19] in their double mass spectrometer and selected ion flow tube (SIFT) study of $OH^- \cdot H_2O$ and NO_2. Three of the reactions they observed were:

$$OH^- \cdot H_2O + NO_2 \longrightarrow HNO_3^- + H_2O \qquad (1)$$

$$\longrightarrow NO_2^- + H_2O + OH \qquad (2)$$

$$\longrightarrow NO_2 + OH^- + H_2O \qquad (3)$$

Their results also indicated that once the HNO_3^- was formed it broke down via electron detachment or dissociation into NO_2^- and OH around interaction energies of 0.8eV. The dissociation of HNO_3^- into OH^- and NO_2 was concluded to be a less likely loss process.

$$HNO_3^- \longrightarrow HNO_3 + e^- \qquad (4)$$

$$\longrightarrow NO_2^- + OH \qquad (5)$$

$$\longrightarrow NO_2 + OH^- \qquad (6)$$
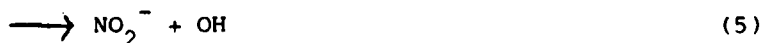
These reactions were chosen since thermodynamic data is available for all of them and they involve many of the species considered above.

COMPUTATIONAL DETAILS

The calculations were carried out ab initio using the Guassian 80 computer program[20] on a DEC VAX 11/780 computer. Moller-Plesset perturbation theory[21] terminated at the second (MP2) and third (MP3, for OH and OH$^-$ only) order was applied to compute electron correlation effects. For OH and OH$^-$ corrections to the Hartree Fock (HF) energy were computed also utilizing a configuration interaction method including all double substitutions (CID). The unrestricted MP method was employed for open-shell systems; the restricted MP method was employed for closed-shell systems. The frozen core approximation, where only valence-shell orbitals are correlated, was used throughout the calculations.

Several different basis sets were utilized in the work. The 4-31G basis is an s,p split valence basis set.[22] 6-31G* is similar but includes also polarization functions of d type on atoms other than hydrogen.[23] The 6-31G* basis set augmented with p-functions on the hydrogens is denoted 6-31G**;[24] 6-311G** is a triple-valence s,p,d basis set.[25] When diffuse sp functions on atoms other than hydrogen are included in the basis set, the symbol + appears in its designation, i.e., 4-31+G.[26]

Standard scale factors and exponents were employed for all basis functions other than the diffuse functions. The scale factor for the diffuse functions was 1.0. The exponent for the diffuse functions added to nitrogen was 0.053 and to oxygen was 0.068.[26] These exponents yielded better results than those suggested by Dunning and Hay (0.048 for nitrogen and 0.059 for oxygen).[27] For molecules containing both nitrogen and oxygen, calculations were carried out with and without diffuse functions on the nitrogen.

The geometries of the molecules and ions were optimized via the Fletcher-Powell method[28] to minimize the total energies. Reported bond lengths represent convergence

to 0.001 Å and bond angles to 0.1°. The total energies were then used to compute electron affinities (E.A.) and bond dissociation energies (D) according to the following equations.

$$E.A.(B) = E(B) - E(B-) \qquad (7)$$

$$D(AB) = E(B) + E(A) - E(AB) \qquad (8)$$

No zero-point corrections are made for any of the calculated energies unless otherwise stated.

STATUS OF RESEARCH

OH, OH⁻. The structures and energies of OH and OH⁻ and the adiabatic electron affinity of OH obtained at the various basis set levels utilized in this work are presented in Tables I and II. These data are compared with the experimental and with other theoretical results in the tables. The structures of these species and of all the other species considered in this study are optimized at the basis set noted unless stated otherwise. The following abbreviations are employed in the tables: DZP, a basis set of double-zeta quality which includes polarization functions; CEPA, coupled electron pair approach to the treatment of electron correlation; PNO-CI, configuration interaction treatment based on pseudo natural orbital configuration expansion; EOM, equations-of-motion technique for calculating electron affinities; CGTO, contracted Gaussian type orbitals.

The results show the following: 1) Including correlation in the basis set lengthens the O-H bond lengths while including polarization functions shortens them. They are shortened more when polarization functions on hydrogen are included than when they are not. 2) When diffuse functions are added to the split-valence s,p basis, the O-H bonds are shortened; however, when they are added to an s,p,d basis, the O-H bond lengths are essentially unchanged. 3) All of the split-valence HF optimi-

TABLE I. Theoretical and Experimental Structures, Energies and Election Affinities of OH.

Method	ROH (Å)	Energy (hartrees)	Electron Affinity (eV)
MNDO[a]	0.937	—	0.27
HF/STO-3G[b]	1.014	-74.36489	-8.16
HF/3-21G[b]	0.986	-74.97023	-2.77
RHF/DZP[c]	0.958	-75.39980	1.03
PNO-CI/DZP+[d]	—	—	1.27[e]
CEPA/DZP+[d]	—	—	1.51[e]
SCF-CI/DZP[f]	0.970(assumed)	—	1.19
SCF-EOM/DZP[f]	0.970(assumed)	—	1.46
HF/6-31G*[b]	0.959	-75.38228	-1.52
MP2/6-31G*[g]	0.979	-75.52103	-0.22
MP3/6-31G*[g]	0.981	-75.53300	-0.44
CID/6-31G*[h]	0.980	-75.53085	-0.52
MP2/6-311G**[h]	0.967	-75.57290	0.019
HF/4-31+G[h]	0.955	-72.77317	0.090
MP2/4-31+G[h]	0.986	-75.38242	1.61
MP2/6-31+G[h]	0.991	-75.46104	1.58
HF/6-31+G*[h]	0.959	-75.38705	-0.26
MP2/6-31+G*[h]	0.981	-75.52931	1.68
MP3/6-31+G*[h]	0.982	-75.54069	1.14
CID/6-31+G*[h]	0.981	-75.53633	1.11
MP2/6-31+G**[h]	0.973	-75.54050	1.74
MP2/6-31+G**(5D)[h]	0.974	-75.53862	1.73
Expt.	0.971[i]	-75.780[j]	1.83[k]

[a]Reference 29. [b]Reference 30. [c]Reference 31. [d]Reference 32. [e]Corrected for zero-point energies. [f]Reference 33. [g]Reference 34. [h]This work. [i]Reference 35. [j]Reference 36. [k]Reference 37.

TABLE II. Theoretical and Experimental Structures and Energies of OH⁻.

Method	ROH (Å)	Energy (hartrees)
MNDO[a]	0.939	—
HF/STO-3G[b]	1.068	-74.06502
HF/3-21G[b]	1.029	-74.86863
RHF/DZP[c]	0.955	-75.36650
PNO-CI/DZP+[d]	0.956	-75.67423
CEPA/DZP+[d]	0.961	-75.69325
HF/6-31G*[b]	0.962	-75.32660
MP2/6-31G*[e]	0.981	-75.51314
MP3/6-31G*[e]	0.981	-75.51703
CID/6-31G*[e]	0.980	-75.51165
MP2/6-311G**[e]	0.968	-75.57360
HF/4-31+G[e]	0.951	-72.77648
MP2/4-31+G[e]	0.988	-75.44139
MP2/6-31+G[e]	0.993	-75.51892
HF/6-31+G*[e]	0.953	-75.37758
MP2/6-31+G*[e]	0.978	-75.59099
MP3/6-31+G*[e]	0.972	-75.58250
CID/6-31+G*[e]	0.972	-75.57701
MP2/6-31+G**[e]	0.971	-75.60427
MP2/6-31+G**(5D)[e]	0.971	-75.60197
Expt.	0.970[f]	-75.847[g]

[a]Reference 29. [b]Reference 30. [c]Reference 31. [d]Reference 32. [e]This work.

[f]Reference 35. [g]Reference 36.

zations yield bond lengths that are too short compared to the experimental values. 4) All of the MP and CID values are too long, with the exception of the case where correlation, diffuse functions, and polarization functions on all atoms are incorporated in the calculations, i.e. MP2/6-31+G**. The latter values are within the experimental uncertainties of the observed values. 5) The MP2/4-31+G bond lengths are too long by approximately 0.02Å. 6) The MP2 technique yielded geometries that are as good or better and electron affinities that are better than those obtained from the MP3 or CID techniques. 7) There is not necessarily a correlation between more stable total energy and more accurate electron affinities. 8) Adding diffuse functions to an s,p,d split-valence basis set improves the accuracy of the calculated electron affinities approximately as much as adding electron correlation does. 9) All of the calculated electron affinities are too low implying that the negative ion is not represented well enough and that zero-point corrections are important for these systems. 10) For this work, only the electron affinity of OH computed at the MP2/6-31+G** and MP2/4-31+G levels are reasonable. These values differ from the experimental value by 0.1eV and 0.2eV, respectively. 11) Polarization functions are not necessary to attain reasonable electron affinities. 12) The electron affinities obtained from this work are as good or better than other values obtained from theoretical calculations reported in the literature. 13) No improvement in the results is achieved by using the MP2/6-31+G basis rather than the MP2/4-31+G basis, by expressing the polarization functions in term of six d-orbitals rather than five, or by employing a triple-valence basis set (MP2/6-311G**).

Atomic charges from population analysis[38] for OH and OH$^-$ and dipole moments for OH at several basis set levels are given in Tables III and IV, respectively. For OH, all of the calculated charge separations are too large since the dipole moments are too large. This is expected to be true for OH$^-$ and all of the other species studied as well. The agreement between the theoretical and experimental dipole moments is improved by adding polarization functions to the basis.

TABLE III. Atomic Charges and Dipole Moment for OH

Method	Charge on O	Charge on H	Dipole Moment (debyes)
HF/6-31G*[a]	-0.444	0.444	1.88
MP2/6-31G*[b]	-0.442	0.442	1.90
MP2/6-311G**[c]	-0.252	0.252	1.83
MP2/4-31+G[c]	-0.408	0.408	2.23
MP2/6-31+G[c]	-0.416	0.416	2.27
HF/6-31+G*[c]	-0.473	0.473	1.96
MP2/6-31+G*[c]	-0.471	0.471	2.01
MP2/6-31+G**[c]	-0.364	0.364	1.96
Expt.[d]	—	—	1.66

[a]Reference 30.   [b]Reference 34.   [c]This work.   [d]Reference 39.

TABLE IV. Atomic Charges for OH⁻

Method	Charge on O	Charge on H
HF/6-31G*[a]	-1.206	0.206
MP2/6-31G*[b]	-1.200	0.200
MP2/6-311G**[c]	-1.063	0.063
MP2/4-31+G[c]	-1.269	0.269
MP2/6-31+G[c]	-1.282	0.282
HF/6-31+G*[c]	-1.351	0.351
MP2/6-31+G*[c]	-1.343	0.343
MP2/6-31+G**[c]	-1.241	0.241

[a]Reference 30.   [b]Reference 34.   [c]This work.

Based on these results, it was decided to consider only two basis sets, where feasible, for the species remaining to be investigated, i.e. MP2/4-31+G and MP2/6-31+G**. The latter basis includes five d-orbitals.

NH, NH⁻. Structures and energies of NH and NH⁻ and adiabatic electron affinities of NH are given in Tables V and VI. The charge distributions obtained from the MP2/4-31+G and MP2/6-31+G** (in parentheses) calculations are given below.

$$
\begin{array}{cc}
(-0.243) & (0.243) \\
N \; — \; H \\
-0.234 & 0.234
\end{array}
\qquad
\left[
\begin{array}{cc}
(-1.136) & (0.136) \\
N \; — \; H \\
-1.123 & 0.123
\end{array}
\right]^{-}
$$
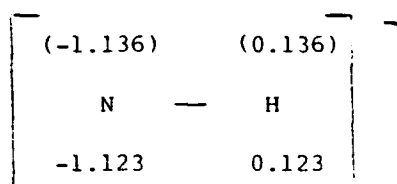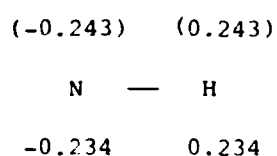
The dipole moment of NH computed at the MP2/6-31+G** level is 1.82D. Several observations can be made upon examining the data in Tables V and VI and in the above figures. 1) The MP2/4-31+G bond length is about 0.01Å too long for NH and 0.02Å too long for NH⁻ compared to their experimental values. 2) The MP2/6-31+G** bond length is within experimental error for NH and about 0.01Å too long for NH⁻. 3) All of the calculated electron affinities are too low, with the best value from this work too low by 0.5eV. The MP2/6-31+G** and MP2/4-31+G values vary by about 0.1eV. 4) Since it is unlikely that zero-point corrections to the energies will improve the theoretical results by 0.5eV, a more accurate basis set is required to properly describe the electron delocalization in NH⁻. 5) The above results imply that the charge separations from population analysis are too large. 6) The polarization functions have very little effect on the charge distributions of these systems.

NH₂, NH₂⁻. Bond lengths, bond angles, and total energies of NH₂ and NH₂⁻ and adiabatic electron affinities of NH₂ are tablulated in Tables VII and VIII. MP2/4-31+G and MP2/6-31+G** (in parentheses) charge distributions are shown below.

$$
\begin{array}{c}
(0.536) \;_{N}\; -0.599 \\
\diagdown \;\;\; \diagup \\
H \qquad\quad H \\
(0.268) \qquad 0.299
\end{array}
\qquad
\left[
\begin{array}{c}
(-1.340) \;_{N}\; -1.392 \\
\diagdown \;\;\; \diagup \\
H \qquad\quad H \\
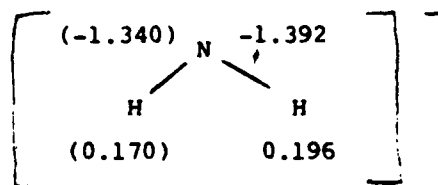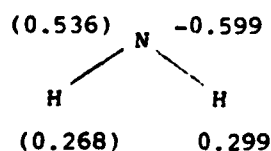(0.170) \qquad 0.196
\end{array}
\right]^{-}
$$

TABLE V. Theoretical and Experimental Structures, Energies and Electron Affinities of NH.

Method	R_{NH} (Å)	Energy (hartrees)	Electron Affinities (eV)
MNDO[a]	0.993	—	-0.78
HF/DZP+[b]	—	—	-1.43[c]
PNO-CI/DZP+[b]	—	—	-0.25[c]
CEPA/DZP+[b]	—	—	0.01[c]
MP2/4-31+G[d]	1.046	-54.94256	-0.220
MP2/6-31+G**[d]	1.035	-55.06980	-0.151
Expt.	1.036[e]	—	0.38[f]

[a]Reference 29. [b]Reference 32. [c]Corrected for zero-point energies. [d]This work.

[e]Reference 35. [f]Reference 40.

TABLE VI. Theoretical and Experimental Structures and Energies of NH$^-$.

Method	R_{NH} (Å)	Energy (hartrees)
MNDO[a]	1.000	—
HF/DZP+[b]	1.022	-54.92219
PNO-CI/DZP+[b]	1.033	-55.12025
CEPA/DZP+[b]	1.039	-55.13703
MP2/4-31+G[c]	1.058	-54.93448
MP2/6-31+G**[c]	1.044	-55.06426
Expt.[d]	1.037	—

[a]Reference 29. [b]Reference 32. [c]This work. [d]Reference 41.

TABLE VII. Theoretical and Experimental Structures, Energies, and Electron Affinities of NH_2.

Method	R_{NH} (Å)	$\Theta_{H\,NH}$ (°)	Energy (hartrees)	Electron Affinity (eV)
CNDO[a]	1.016	105.4	—	0.61
MNDO[b]	1.002	104.4	—	-0.44
CGTO/DZP+[c]	1.016	105.4	—	0.61
MP2/4-31+G[d]	1.029	108.8	-55.56300	0.387
MP2/6-31+G**[d]	1.025	104.0	-55.71336	0.464
Expt.	1.024[e]	103.3[e]	—	0.779[f]

[a]Reference 42. [b]Reference 29. [c]Reference 43. [d]This work. [e]Reference 44.

[f]Reference 45.

TABLE VIII. Theoretical and Experimental Structures and Energies of NH_2^-.

Method	R_{NH} (Å)	$\Theta_{H\,NH}$ (°)	Energy (hartrees)
MNDO[a]	1.013	100.9	—
CGTO/DZP+[b]	1.016	103.9	—
MP2/4-31+G[c]	1.037	107.7	-55.57728
MP2/6-31+G**[c]	1.029	103.7	-55.73041
Expt. (solid)[d]	1.03	104	—

[a]Reference 29. [b]Reference 44. [c]This work. [d]Reference 46.

TABLE VII. Theoretical and Experimental Structures, Energies, and Electron Affinities of NH_2.

Method	R_{NH} (Å)	$\Theta_{H\,NH}$ (°)	Energy (hartrees)	Electron Affinity (eV)
CNDO[a]	1.016	105.4	—	0.61
MNDO[b]	1.002	104.4	—	-0.44
CGTO/DZP+[c]	1.016	105.4	—	0.61
MP2/4-31+G[d]	1.029	108.8	-55.56300	0.387
MP2/6-31+G**[d]	1.025	104.0	-55.71336	0.464
Expt.	1.024[e]	103.3[e]	—	0.779[f]

[a]Reference 42. [b]Reference 29. [c]Reference 43. [d]This work. [e]Reference 44.

[f]Reference 45.

TABLE VIII. Theoretical and Experimental Structures and Energies of NH_2^-.

Method	R_{NH} (Å)	$\Theta_{H\,NH}$ (°)	Energy (hartrees)
MNDO[a]	1.013	100.9	—
CGTO/DZP+[b]	1.016	103.9	—
MP2/4-31+G[c]	1.037	107.7	-55.57728
MP2/6-31+G**[c]	1.029	103.7	-55.73041
Expt. (solid)[d]	1.03	104	—

[a]Reference 29. [b]Reference 44. [c]This work. [d]Reference 46.

The MP2/6-31+G** dipole moment of NH_2 is 2.21D.

The following conclusions can be drawn from the tables and figures. 1) The N-H bond lengths are reproduced very well at both basis set levels for NH_2 and NH_2^-. 2) These basis sets yield bond lengths closer to the experimental values than the other theoretical results reported. 3) The agreement between the experimental and calculated bond angles is also very good at the MP2/6-31+G** level for both species. However, the MP2/4-31+G bond angles are too large. 4) The best electron affinity obtained from this work is approximately 0.3eV lower than the experimental value and 0.15eV lower than the best theoretical value. The two electron affinities computed from this research vary by about 0.1eV. 5) These calcualted electron affinities are 0.2eV closer to the experimental result than they are for NH.

H_2O. Optimized structures and total energies for H_2O are presented in Table IX. Charge distributions from population analysis are given in the figures below for the MP2/4-31+G and MP2/6-31+G** (in parentheses) basis sets. The experimental dipole moment for H_2O is 1.85D[39] and the MP2/6-31+G** value is 2.28D.
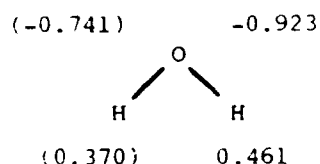
```
(-0.741)        -0.923
            O
          /   \
        H       H
     (0.370)      0.461
```

TABLE IX. Theoretical and Experimental Structures and Energies of H_2O.

Method	R_{OH} (Å)	Θ_{HOH} (°)	Energy (hartrees)
CNDO/2[a]	1.04	104.5	-19.892
RHF/DZP[b]	0.947	105.2	-76.0410
HF/4-31++G[c]	0.956	106.6	-75.94946
MP2/4-31+G[d]	0.969	111.7	-76.04841
MP2/6-31+G**[d]	0.964	105.5	-76.23042
Expt.[e]	0.957	104.5	——

[a]Reference 47. [b]Reference 31. [c]Reference 48. The 4-31G basis set was augmented with two uncontracted diffuse s functions on each hydrogen and nine sets of uncontracted diffuse s and p functions on oxygen. [d]This work. [e]Reference 49.

The results show: 1) The MP2/4-31+G and MP2/6-31+G** optimized O-H bond lengths are about 0.01 Å too long and the optimized H-O-H bond angle is about 7° too large for the former basis set computation. 2) The calculated charge separations are too large.

OOH, OOH⁻. Geometries and energies of OOH and OOH⁻ and the adiabatic electron affinity of OOH are shown in Tables X and XI. Atomic charges obtained from the MP2/4-31+G and MP2/6-31+G** (in parentheses) calculations are displayed below. The computed dipole moment (MP2/6-31+G**) of OOH is 2.15D.

```
(-0.0297) (-0.363) (0.392)                  ⌈ (-0.728) (-0.588) (0.316) ⌉⁻
                                            |                            |
   O ——— O ——— H                            |   O ——— O ——— H            |
                                            |                            |
  0.00200  -0.471   0.469                   ⌊ -0.628    -0.733    0.361  ⌋
```

From the data in the tables and figures it is evident that: 1) The MP2/6-31+G** and experimental bond lengths and bond angles for OOH are very close, whereas the MP2/4-31+G values are too large by 0.05Å (O-O), 0.01Å (O-H) and 2°. 2) For OOH⁻, the MP2/4-31+G calculated O-O distance varies from the MP2/6-31+G** distance by 0.1Å and the O-H distances vary by 0.015Å. The O-O-H bond angles are similar. 3) It is necessary to include polarization functions in the basis set for a proper description of the O-O bond. 4) This is the first case where the electron affinity is too high (by 0.3eV) when d-functions are not included in the basis set and too low (by 0.1eV) when they are. Incorporating polarization functions stabilizes the neutral OOH molecule more than the OOH⁻ ion which decreases the magnitude of the theoretically determined electron affinity. For all of the other species considered above, the anion was stabilized more than the neutral system. 5) The negative charge is delocalized more at the MP2/4-31+G level of calculation but for both levels most of the additional negative charge in OOH⁻ is on the terminal oxygen (0.6 - 0.7e).

TABLE X. Theoretical and Experimental Structures, Energies, and Electron Affinities of OOH.

Method	R_{OO} (Å)	R_{OH} (Å)	Θ_{OOH} (°)	Energy (hartrees)	Electron Affinities (eV)
INDO[a]	1.185	1.047	110.6	—	—
CI/DZ[b]	1.458	0.973	104.6	-150.2448	—
MP2/4-31+G[c]	1.385	0.985	106.9	-150.19329	1.49
MP2/6-31+G**[c]	1.329	0.977	104.7	-150.51427	1.06
Expt.	1.335[d]	0.977[d]	104.1[d]	—	1.19[e]

[a]Reference 50.   [b]Reference 51.   [c]This work.   [d]Reference 44.   [e]Reference 52.

TABLE XI. Theoretical and Experimental Structures and Energies of OOH⁻

Method	R_{OO} (Å)	R_{OH} (Å)	Θ_{OOH} (°)	Energy (hartrees)
HF/STO-3G[a]	1.449	1.021	105.4	-147.93655
MP2/4-31+G[b]	1.610	0.980	96.6	-150.24786
MP2/6-31+G**[b]	1.516	0.966	97.3	-150.55336

[a]Reference 30.   [b]This work.

OH⁻·H₂O. Table XII gives optimized structures and total energies of $OH \cdot H_2O^-$. One point of interest with respect to the geometry of this ion is whether it is symmetric or not. Earlier studies have shown that calculations carried out with a limited basis set[47,53,54] and/or only partial geometry optimization[54,55] are not sufficiently accurate to settle this point. Later work[56] undertaken by performing a global geometry optimization with a correlated wavefunction indicates that this anion is symmetric. However, no diffuse functions were included in the basis set of any of these prior calculations, and diffuse functions are known to be important for a proper description of anionic species.[26,27] The preliminary MP2/4-31+G fully optimized results imply that cis, trans, and gauche $OH^- \cdot H_2O$ are asymmetric with an O-O bond length of about 2.6Å and with the central hydrogen moving about 0.08Å along the O-O bond axis. However, the structural data obtained for OOH and OOH⁻ suggest that these bond lengths are too long. Since it is widely accepted now that a hydrogen bond will be symmetric when the distance between the heavy atoms is less than 2.50Å[58] and the corrected O-O bond distance will be close to this value, an even more accurate basis set (i.e., MP2/6-31+G**) is required to resolve this question. In addition, other conformations must be considered since Rohlfing et.al.[56] find that the dihedral angle defined by the external hydrogen is 110°.

At the MP2/4-31+G level of calculation, the trans and gauche systems are of essentially equal energy, and they are more stable than the cis system by 1.70 kcal. All three systems have slightly non-linear hydrogen bonds with the central hydrogen 5.3°, 6.1°, and 1.9° above the O-O bond axis in the gauche, trans, and cis forms, respectively. The bonds between the oxygens and terminal hydrogens have remained essentially constant in length (to within 0.01Å) compared to their values in OH⁻ and H₂O and the H-O-H angle has decreased by about 3°. These results are consistent with Rohlfing et al's. work[56] and with results from other studies of asymmetric hydrogen bonds.[58]

The adiabatic electron affinity of $OH \cdot H_2O$ can be computed from the MP2/4-31+G total energies of $OH^- \cdot H_2O$, OH, and H_2O by assuming that the bond dissociation energy (D) of $OH \cdot H_2O$ is negligible. The number obtained is 2.86eV which is in good agreement with the experimental value of 2.91eV.[19] The latter is derived from E.A. (OH) and D $(OH^- \cdot H_2O)$ assuming D $(OH \cdot H_2O)$ is negligible.

A comparison of the charge distributions calculated at the MP2/4-31+G level for OH^-, H_2O and trans $OH^- \cdot H_2O$ (given below) shows that there is a transfer of only $0.0500e^-$ from the OH^- to the H_2O upon formation of the hydrogen bond. The electron density is transferred to the oxygen and terminal hydrogen of the water. However, most of the gain in electron density on these two atoms comes from the central hydrogen which loses $0.129e^-$ when the hydrogen bond is formed. Similar charge redistributions were found for the cis and gauche structures and in other studies of hydrogen bonded systems.[58]
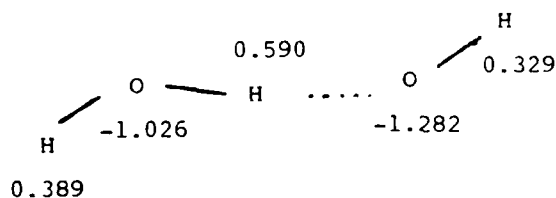

NO_2, NO_2^-. Structures and energies of NO_2 and NO_2^- and electron affinities of NO_2 are tabulated in Tables XIII and XIV. From these tables it is observed that: 1) For NO_2 the MP2/6-31+G** and experimental NO bond lengths differ by 0.025Å and ONO angles differ by $0.4°$. The distance and angle computed at the MP2/4-31+G level are too large by 0.6Å and $0.4°$, respectively. 2) For NO_2^- the MP2/6-31+G** and gas phase experimental NO bond lengths vary by 0.13Å and the ONO angles vary by $3.5°$. The distance calculated at the MP2/4-31+G level is too large by 0.18Å and the angle is too small by $4°$. 3) In all other cases where a comparison can be made, the MP2/6-31+G** and experimental bond lengths differ by no more than 0.04Å. This suggests that the experimentally determined gas phase NO distance may be too short

TABLE XII. Theoretical and Experimental Structures and Energies of $OH^- \cdot H_2O$.

Method	r_1^a (Å)	r_2^a (Å)	r_3^a (Å)	r_4^a (Å)	Θ_1^a (°)	Θ_2^a (°)	ϕ^a (°)	α^a (°)	Energy (hartrees)
CNDO/2(sym)[b,c]	1.04	1.17	1.17	1.04	106	106	180.0	180.0	-38.928
HF/STO-3G(asym)[c,d]	1.007	1.010	1.199	1.163	100.9	101.1	180.0	180.0	-149.14322
HF/4-31G(asym)[c,d]	0.955	1.106	1.348	0.962	108.8	108.0	180.0	180.0	-151.20343
HF/4-31G(sym)[e,f]	0.958	1.212	1.212	0.958	109.2	109.2	180.0	150.0	-151.20325
HF/4-31G(asym)[e,f]	0.955	1.097	1.361	0.962	108.1	110.0	176.1	135.0	-151.20358
HF/6-31G*(asym)[c,d]	0.949	1.095	1.384	0.951	102.6	101.7	180.0	180.0	-151.39246
HF/6-31G*(sym)[e,f]	0.950	1.207	1.209	0.950	102.2	102.2	180.0	120.0	-151.39176
HF/6-31G*(asym)[e,f]	0.948	1.040	1.488	0.953	100.8	101.8	173.2	115.0	-151.39340
HF/6-31G**(asym)[d,g]	0.949	1.095	1.384	0.951	102.6	101.7	180.0	180.0	-151.41148
HF/6-31G**(sym)[e,f]	0.946	1.203	1.206	0.946	102.7	102.7	180.0	120.0	-151.41105
HF/6-31G**(asym)[e,f]	0.944	1.044	1.457	0.949	101.4	102.5	174.?	115.0	-151.41228
CI/DZ(sym)[h,i]	0.958	1.206	1.206	0.958	104.5	104.5	180.0	180.0	-151.72689
CI/DPZ(asym)[h,j]	0.957	1.092	1.373	0.957	104.5	104.5	180.0	180.0	-151.91518
MP2/6-31G**(sym)[e,f]	0.965	1.223	1.223	0.964	99.1	99.1	180.0	110.0	-151.82012
MP2/4-31+G(asym)[k,l]	0.971	1.047	1.561	0.979	108.2	128.3	168.3	180.0	-151.53584
MP2/4-31+G(asym)[k,l]	0.971	1.048	1.558	0.980	108.0	123.9	171.1	60.0	-151.53585
MP2/4-31+G(asym)[k,l]	0.971	1.040	1.586	0.980	108.3	126.0	179.8	0.0	-151.53313
Expt.[m] (solid)	——	1.145	1.145	——	——	——	——	——	——

[a]See figure below for definitions. [b]Reference 47. [c]The hydrogen bond was assumed to be linear and trans. All other geometrical parameters were optimized. [d]Reference 53. [e]All geometrical parameters were optimized. [f]Reference 56. [g]The energy was calculated using the HF/6-31G* optimum structure. [h]The hydrogen bond was assumed to be linear. Only r_2 and r_3 were optimized. The other parameters are taken from experimental values for H_2O. [i]Reference 54. [j]Reference 55. [k]This work. [l]The dihedral angles were fixed at the values given in the table. All other parameters were optimized. [m]Reference 57. The hydrogen bond was assumed to be symmetric.
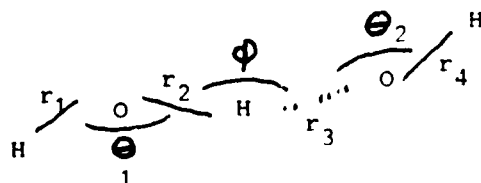
α is the dihedral angle derived from the external hydrogens.

by about 0.10Å. 4) Baird and Taylor[59] find that adding polarization functions to only the nitrogen shortens the N-O bonds. This result implies that optimized geometries obtained using the MP2/4-31+G basis should be improved by adding polarization functions to the nitrogen. It is also possible that this addition will improve the theoretical electron affinities. (It is being tested now.) 5) Including diffuse functions on N in the basis set has little effect on the optimized geometries but does improve the electron affinities. Thus, it is recommended that structures be determined with a basis set which does not incorporate diffuse functions on nitrogen and then that these structures be used to compute a new total energy with a basis which does incorporate these functions. 6) The best MP2/6-31+G** value for the electron affinity is too low by 0.25-0.35eV; the best MP2/4-31+G value is too low by 0.05-0.10eV. Again the electron affinity calculated without polarization functions is larger (by 0.2eV) than that calculated with polarization functions in the basis set. Although a more complete analysis is required, it is possible that there will be a compensatory effect between neglecting polarization functions and zero-point energies for systems containing more than one non-hydrogen atom. 7) The best electron affinity obtained from this work is as good or better than the numbers reported in the literature.

Table XV lists charge distributions of NO_2 and NO_2^- from population analysis and dipole moments of NO_2. It is clear from these data that: 1) The calculated dipole moments are too large. 2) Incorporating diffuse functions on N in the basis set decreases the charge separation in the N-O bonds and slightly improves the dipole moments. 3) Although more of the extra negative charge on NO_2^- is distributed to the oxygens than the nitrogen, the percentage of electron density delocalized on the nitrogen increases to 30% when polarization and diffuse functions on N are incorporated in the basis set. 4) This is the only set of molecules studied thus far where there is a significantly greater charge separation in the N-O bonds and a slightly poorer computed dipole moment when polarization functions are included in the basis than when they are not included.

TABLE XIII. Theoretical and Experimental STructures, Energies, and Electron Affinities of NO_2

Method	R_{NO} (Å)	Θ_{ONO} (°)	Energy (hartrees)	Electron Affinity (eV)
MNDO[a]	1.174	133.0	——	2.55
HF/4-31G[b]	1.19	136.7	-203.69429	1.51
HF/4-31G[N* b]	1.16	135	-203.77780	1.11
SCF-EOM/DZ+[c]	1.21	134	-203.9609	2.25[d]
MP2/4-31+G[e,f]	1.250	133.7	-204.10858	2.14
MP2/4-31+G[e,g]	1.250	133.7	-204.11125	2.21
MP2/6-31+G**[e,f]	1.217	133.7	-204.56441	1.93
MP2/6-31+G**[e,g]	1.217	133.7	-204.56579	2.02
Expt.	1.193[h]	134.1[h]	——	2.275[i]
Expt.	——	——	——	2.36[j]

[a]Reference 29. [b]Reference 59. The N* designates that polarization functions were added to the nitrogen only. [c]Reference 60. [d]Corrected for zero-point energies. [e]This work. [f]Diffuse functions were added to the oxygen only. [g]Diffuse functions were added to the oxygens and nitrogen. The energy was calculated at the optimized geometry obtained without diffuse functions on the nitrogen. [h]Reference 61. [i]Reference 62. [j]Reference 63.
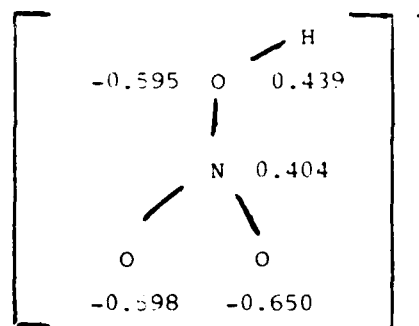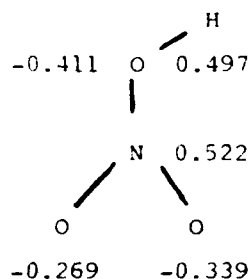
TABLE XIV. Theoretical and Experimental Structures and Energies of NO_2^-.

Method	R_{NO} (Å)	Θ_{ONO} (°)	Energy (hartrees)
MNDO[a]	1.215	116.5	——
HF/4-31G[b]	1.256	117.0	-203.74991
HF/4-31G[N* b]	1.23	116	-203.81844
MP2/4-31+G[c,d]	1.328	115.6	-204.18704
MP2/4-31+G[c,e]	1.328	115.6	-204.19229
MP2/4-31+G[c,f]	1.327	115.8	-204.19229
MP2/6-31+G**[c,d]	1.280	115.7	-204.63531
MP2/6-31+G**[c,e]	1.280	115.7	-204.64003
MP2/6-31+G**[c,f]	1.278	116.0	-204.64005
Expt. (gas)[g]	1.15	119.5	——
Expt. (crystal)[h]	1.236	115.4	——

See footnotes on the following page.

[a]Reference 29. [b]Reference 59. [c]This work. [d]Diffuse functions were added to the oxygens only. [e]Diffuse functions were added to the oxygens and nitrogen. The energy was calculated at the optimized geometry obtained without diffuse functions on the nitrogen. [f]Diffuse functions were added to the oxygens and nitrogen. [g]Reference 62. [h]Reference 64.

HNO_3, HNO_3^-. Table XVI gives optimized geometries and total energies of HNO_3 and planar HNO_3^- and adiabatic electron affinities of HNO_3. Pyramidal structures of HNO_3^- are currently under investigation, and the preliminary data indicate that pyramidal HNO_3^- is the more stable form. The MP2/4-31+G charge distributions for HNO_3 and HNO_3^- are presented below. The calculated dipole moment of HNO_3 is 2.99D; the experimental value is 2.19D.

```
            H                              ┌           H        ┐ ⁻
-0.411  O   0.497                          │ -0.595  O   0.439  │
        |                                  │         |          │
        N   0.522                          │         N   0.404  │
       / \                                 │        / \         │
      O   O                                │       O   O        │
  -0.269  -0.339                           └  -0.?98  -0.650     ┘
```

The following conclusions can be drawn from these results. 1) The optimized bond distances between the nitrogen and terminal oxygens differ from the experimental numbers by 0.04-0.05Å. The other calculated N-O distance is too long by about 0.10Å. The bond angles are within 2° of each other. 2) Based on earlier results, the computed O-H bond is likely to be about 0.015Å too long. 3) Some of the variance in calculated and observed geometries is due to experimental uncertainty. 4) At present the theoretically obtained electron affinity is 0.4eV too low. This error will be improved when the most stable form of HNO_3^- is determined and when diffuse functions on the nitrogen are incorporated in the basis set. It is expected that the error in the computed electron affinity will then be comparable to that found for NO_2.

TABLE XV. Atomic Charges and Dipole Moments for NO_2 and NO_2^-.

Molecule	Method	Charge on N	Charge on O	Dipole Moment (debyes)
NO_2	MP2/4-31+G[a]	0.548	-0.274	0.687
	MP2/4-31+G[b]	0.189	-0.0945	0.672
	MP2/6-31+G**[a]	0.659	-0.329	0.748
	MP2/6-31+G**[b]	0.386	-0.193	0.733
	Expt.[c]	——	——	0.316
NO_2^-	MP2/4-31+G[a]	0.325	-0.662	
	MP2/4-31+G[b]	-0.0303	-0.485	
	MP2/4-31+G[d]	-0.0276	-0.486	
	MP2/6-31+G**[a]	0.403	-0.701	
	MP2/6-31+G**[b]	0.0843	-0.542	
	MP2/6-31+G**	0.0838	-0.542	

[a]Diffuse functions were added to the oxygens only. [b]Diffuse functions were added to the oxygens and nitrogen. The energy was calculated at the optimized geometry obtained without diffuse functions on the nitrogen. [c]Reference 39. [d]Diffuse functions were added to the oxygens and nitrogen.

5) The charge distribution and structure of HNO_3^- enables one to answer the question as to whether it should more properly be considered $OH^- \cdot NO_2$. The atomic charges show that HNO_3^- is the more correct designation since the OH moiety has a total charge of -0.15e. Furthermore, the fact that the bond between the nitrogen and the oxygen of the OH group is only 0.025Å longer in HNO_3^- than in HNO_3 argues that the anion is a covalent compound rather than a complex. 6) Every atom in HNO_3 gains electron density when it is negatively charged, but most of the extra electron density is distributed to the terminal oxygens (0.3e each). 7) As usual the theoretically determined dipole moment is too large.

$H_2NO_4^-$. Earlier work performed in this laboratory led to the conclusion that $OH^- \cdot HNO_3$ cannot be considered a solvated point charge and is more correctly designated as $H_2NO_4^-$. Several possible conformers of this species have been investigated at several basis set levels (Table XVII). The MP2/4-31+G calculation remains to be done. A complete geometry optimization was carried out, with the exception of the O-H bond lengths in conformer II (HF/6-31G* calculation) and conformer III (HF/4-31G calculation). The earlier study revealed that the effect on the total energy of the system of optimizing the O-H bond lengths is negligible compared to the effects of the other parameters. All three conformers have a distorted tetrahedral geometry. Both the HF/4-31G and HF/6-31G* bond lengths are most likely too short, and the bond angles are most likely too large.

From the total energies given in Table XVIII, it is evident that conformer I is only slightly more stable than the other two conformers. The bond dissociation energy, $D(H_2NO_4^-)$, is calculated according to the following equation and is about 0.87eV too low compared to the experimental number.

$$D(H_2NO_4^-) = E(HNO_3) + E(OH^-) - E(H_2NO_4^-)$$

The discrepancy in these values may be due in part to experimental uncertainty, since $D(H_2NO_4^-)$ was never measured directly but was determined from a thermodynamic cycle. In addition, if any conformation not yet considered is more stable than I, the mag-

TABLE XVI. Theoretical and Experimental Structures, Energies, and Electron Affinities of HNO_3 and HNO_3^-.

| Molecule	Method	r_1[a] (Å)	r_2[a] (Å)	r_3[a] (Å)	r_4[a] (Å)	θ[a] (°)	ϕ[a] (°)	α[a] (°)	Energy (hartrees)	Electron Affinity (eV)
HNO_3	HF/4-31G[b]	1.202	1.202	1.421	0.960	115.2	122.4	100.0	-278.38916	—
(planar)	HF/4-31G[c]	1.219	1.194	1.373	0.961	128.9	116.2	107.7	-278.99211	—
	HF/6-31G*[c]	1.188	1.172	1.334	0.955	129.2	116.1	105.3	-279.44426	—
	MP2/4-31+G[c]	1.260	1.250	1.506	0.989	131.1	115.9	104.0	-279.54618	0.15
	Expt.[d]	1.21	1.21	1.41	0.96 (assumed)	130	114	102	—	0.57[e] 0.56[f]
HNO_3^- (planar)	MP2/4-31+G	1.348	1.311	1.530	0.985	132.0	112.9	99.0	-279.55174	—

[a]See figure below for definitions. [b]Reference 65. r_1 and r_2 were constrained to be identical. [c]This work. Diffuse functions were added to the oxygens only. [d]The structural data is from reference 66. r_1 and r_2 were assumed to be identical. [e]Reference 67. [f]Reference 19.
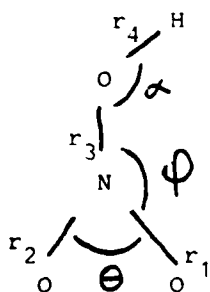
nitude of the theoretically computed $D(H_2NO_4^-)$ would increase.

Adding polarization functions to the basis set worsens the agreement between the theoretically and experimentally obtained bond dissociation energies. Taking correlation into account improves the agreement between them. Thus, the polarization functions stabilize the fragments more than $H_2NO_4^-$ while the reverse is true for the correlation effects.

HF/6-31G* atomic charges are displayed for HNO_3 and conformer I of $H_2NO_4^-$ in the figure below. Several observations can be made upon examining this figure. 1) 0.811e has been transferred from the OH^- to the HNO_3 group in the ion. 2) The negative charge has been distributed over all of the atoms in the HNO_3 moiety; each atom is more negative in the ion than it is in HNO_3.


I
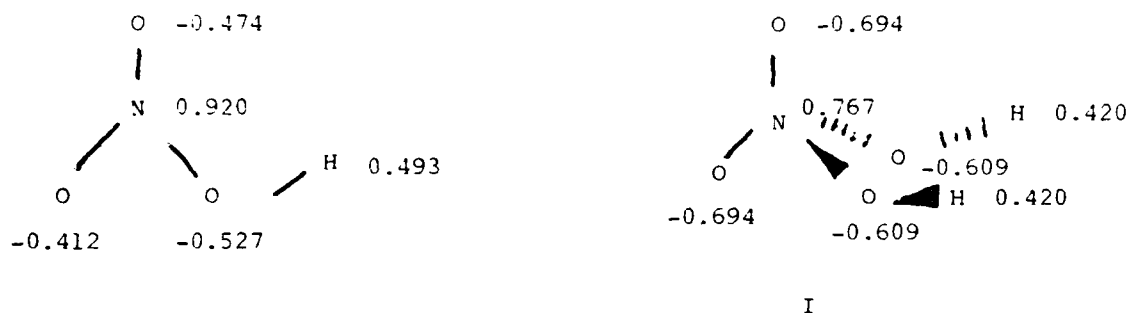
Thermodynamic data. Table XIX lists thermodynamic data for several reactions involving some of the species studied. Neither zero-point nor termperature correct-ions have been made in the ΔE values, unless otherwise indicated. Where possible the ΔE's have been compared at several different basis set levels. The results show that 1) The ΔE's for the reactions involving HNO_3^- do not agree well with the ΔH's for these reactions, since the structure of HNO_3^- has not been completely optimized yet. 2) The ΔE's, computed from the MP2/4-31+G data, for the other reactions are all within 0.2eV of the ΔH's. 3) The variance between the ΔH's and ΔE's calculated at the MP2/6-31+G** level is larger, again suggesting that there

TABLE XVII. Theoretical Structure of $H_2NO_4^-$.[a]

Parameters[b]	$H_2NO_4^-$, I	$H_2NO_4^-$, II	$H_2NO_4^-$, III[c]
$N-O_1$	1.343 (1.284)	1.375 (1.307)	1.342
$N-O_2$	1.343 (1.284)	1.314 (1.264)	1.336
$N-O_3$	1.457 (1.430)	1.459 (1.431)	1.455
$N-O_4$	1.457 (1.430)	1.459 (1.431)	1.455
O_3-H_5	0.957 (0.950)	0.957 (0.949)	0.957
O_4-H_6	0.957 (0.950)	0.957 (0.949)	0.957
$\angle O_1NO_2$	120.5 (120.2)	119.8 (119.6)	116.9
$\angle O_1NO_3$	109.2 (108.8)	110.9 (110.1)	110.2
$\angle O_1NO_4$	107.1 (107.6)	110.9 (110.1)	110.2
$\angle NO_3H_5$	100.9 (99.2)	100.9 (99.0)	101.1
$\angle NO_4H_6$	101.0 (99.2)	100.9 (99.0)	101.1
$\angle O_1O_2NO_3$	124.5 (124.8)	123.4 (124.0)	126.0
$\angle O_1O_2NO_4$	234.6 (-124.8)	236.5 (236.0)	234.0
$\angle O_1NO_3H_5$	-12.5 (-16.0)	0.4 (0.0)	59.7
$\angle O_1NO_4H_6$	214.6 (212.7)	-0.4 (0.0)	300.3

[a] Bond lengths are in Å, bond angles are in degrees. The values in parentheses are the HF/6-31G* optimized values; the others are the HF/4-31G values. [b] See the figure below for definitions. [c] The geometry of conformer III was not optimized using the HF/6-31G* basis set since it is the least stable of the three.
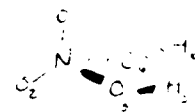
TABLE XVIII. Total Energy and Bond Dissociation Energy of $H_2NO_4^-$.

System	Method	E_{tot} (hartrees)	$D(H_2NO_4^-)$ (eV)
$H_2NO_4^-$, I	HF/4-31G	-354.30674	2.31
	HF/6-31G*	-354.82468	1.47
	MP2/6-31G*//HF/6-31G*[a]	-355.76110	2.55[b]
$H_2NO_4^-$, II	HF/4-31G	-354.30377	
	HF/6-31G*	-354.82241	
$H_2NO_4^-$, III	HF/4-31G	-354.30067	
Expt.[c]		——	3.5

[a] The total energy was calculated at the MP2/6-31G* level using the optimized geometry obtained at the HF/6-31G* level. [b] This number was computed using $E(HNO_3) = -280.15453$ a.u. and $E(OH^-) = -75.51286$ a.u., i.e. their MP2/6-31G*//HF/6-31G* values. [c] Reference 17a.

TABLE VIX. Thermodynamic Data

Reaction	Method (for ΔE)	ΔE(eV/mole)	ΔH(eV/mole)
1. $OH^- \cdot H_2O + NO_2 \rightarrow HNO_3^- + H_2O$	MP2/4-31+G[a]	1.21	0.23(estimated)[b]
2. $OH^- \cdot H_2O + NO_2 \rightarrow NO_2^- + H_2O + OH$	MP2/4-31+G[a]	0.72	0.63[d]
	MP2/4-31+G[c]	0.65	
	MP2/6-31+G**[a]	0.97	
	MP2/6-31+G**[c]	0.88	
3. $OH^- \cdot H_2O \rightarrow OH^- + H_2O$	MP2/4-31+G	1.25(1.11)[e]	1.08[f]
	MP2/6-31+G**	1.17(1.03)[e]	
	HF/6-31G**//HF/6-31G*[g]	1.50(1.37)[e]	
	HF/4-31+G[h]	1.19	
4. $HNO_3^- \rightarrow NO_2 + OH^-$	MP2/4-31+G[a]	0.049	0.87(estimated)[b]
5. $HNO_3^- \rightarrow NO_2^- + OH$	MP2/4-31+G[a]	-0.48	0.43(estimated)[b]
6. $OH^- + NO_2 \rightarrow NO_2^- + OH$	MP2/4-31+G[a]	-0.53	-0.44(estimated)[b]
	MP2/4-31+G[c]	-0.59	
	MP2/6-31+G**[a]	-0.20	
	MP2/6-31+G**[c]	-0.29	

[a] Diffuse functions have been added to the oxygens only. [b] J.F. Paulson, personal communication. These values were not measured directly but were calculated from a thermodynamic cycle. [c] Diffuse functions have been added to the oxygens and nitrogens. [d] Reference 19. [e] The values in parentheses have been corrected for zero-point energies. [f] Reference 17b. [g] Reference 53. [h] R.R.Squires, personal communication to J.F. Paulson.

is some cancellation of errors when zero-point energies and polarization functions are neglected. 4) The results are particularly good for $D(OH^- \cdot H_2O)$, which is encouraging since bond dissociation energies are often poorly represented at lower levels of theory.[10,26,58]

SUMMARY

1) At the MP2/4-31+G level, all calculated bond lengths are too long and all calculated bond angles are too large (with the exception of NO_2 and NO_2^-) compared to their experimental values and their values obtained with bigger basis sets. XH, where X = N, O, bond lengths are too long by 0.01 - 0.02Å, with the difference being closer to 0.01Å for the neutral systems and to 0.02Å for the negative ions. XX and XY bond lengths are too long by 0.05 - 0.10Å, again the smaller error is associated with the neutral systems and the larger error with the anions. The discrepancies in the bond angles range from $0.5°$ to $7°$. The worst disagreements occur for the XH_2 systems. Poor experimental data for some of these species accounts, at least partially, for the large magnitude of some of these error ranges.

2) Except for NO_2 and NO_2^-, the MP2/6-31+G** optimized bond distances and angles are within 0.007Å and $0.5°$ respectively, of the observed values. Again, poor experimental data may explain the poor theoretical results for NO_2^-.

3) Electron affinities and other thermodynamics data computed at the MP2/6-31+G** and MP2/4-31+G basis set levels are in reasonable agreement with the experimental numbers. For the electron affinities, the biggest disagreement is for NH, 0.5eV. Apparently, one set of diffuse functions on the nitrogen is not sufficient to obtain accurate results for NH. However, as the size of the nitrogen-containing species increases and the electron density is more delocalized, the agreement between the theoretical and experimental values improves. Overall, the calculated electron affinities are as good or better than most of the other calculated values reported in the literature.

4) Even though it appears that the errors in the theoretical thermodynamic

data arising from neglecting zero-point energies may be partially canceled by the errors arising from neglecting polarizing functions, a complete assessment of the usefulness of these calculations in predicting thermodynamic data cannot be made until zero-point energy effects have been evaluated.

5) Adding polarization functions to the basis set gives rise to shorter optimized bond lengths and smaller optimized bond angles, even when the polarization functions are incorporated only on the central atom. Taking correlation effects into account produces longer optimized bond lengths and smaller optimized bond angles. (See references 30 and 34, also.) Including diffuse functions in the basis has little effect on either the bond distances or angles. In contrast, all three of these factors lead to improve theoretical electron affinities and reaction energies. Combining these results suggests that the geometries of these species should be calculated utilizing either the MP2/4-31G or MP2/4-31G* basis set, with polarization functions on the central atom only. Then the total energies should be computed at the MP2/4-31+G or preferably, where possible, at the MP2/6-31+G** level using the previously determined optimized geometries.

6) The preliminary MP2/4-31+G results indicate that $OH^- \cdot H_2O$ is asymmetric but additional work using this and the MP2/6-31+G** basis is required to settle this question. It is possible that the asymmetric structure is a local minimum on the potential energy surface rather than the true minimum and that the relative energies of the symmetric and asymmetric forms of $OH^- \cdot H_2O$ may change when the more accurate calculations are carried out.[56]

7) Although the final optimized geometry of HNO_3^- has not been determined yet, HNO_3^-, unlike HNO_3, has a pyramidal structure. The thermodynamic data for reactions involving HNO_3^- will improve when its optimum geometry and total energy are obtained.

8) $H_2NO_4^-$ has a distorted tetrahedral geometry. Several conformers may very similar energies. Further work necessary to improve the ΔE's for reactions this anion undergoes.

9) Where a comparison can be made, all of the calculated dipole moments are too large by 0.3 - 0.8D compared to the experimental values. This indicates that the computed charge separations are too large.

FOLLOW-ON RESEARCH

Specific recommendations for follow-on research include:

1) Optimizing the structures of all the species considered in the present study utilizing the MP2/4-31G and MP2/4-31G* basis sets to asses their reliability compared to that of the MP2/6-31+G** and MP2/4-31+G basis sets. If the former two basis sets do yield reliable results, considerable computer time could be saved in carrying out further studies of this type.

2) Calculating the zero-point energies of all the species considered in the present study. This will be done using the new GAUSSIAN 82 program which should be available shortly.

3) Using isodesmic reactions, i.e. reactions where the number of bonds of a given type are retained,[68] to compute electron affinities and other thermodynamic data. This type of approach often reduces inaccuracies in calulated reaction energies.[68,69]

4) Continuing the investigation of the structure of $OH^- \cdot H_2O$ to determine whether the hydrogen bond is symmetric or asymmetric and to compare the results at various levels of theory. This will entail finding the optimum geometry of $OH^- \cdot H_2O$ at the MP2/4-31+G and MP2/6-31+G** levels.

5) Completing the MP2/4-31+G optimization of pyramidal HNO_3^-. Then this geometry will be used, i.e. no additional optimizations will be performed, to find the effect on the total energy of HNO_3^- of adding polarization and diffuse functions to the nitrogen.

6) Employing the most accurate basis set possible, within feasible economic and time constraints, to determine the otpimal structure and total energy of $H_2NO_4^-$

and H_2NO_4. These data would be used then to obtain bond dissociation energies and electron affinities for these species.

7) Extending this research to include other anions, in particular other nitrogen oxides.

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PUBLICATIONS

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2. "The Role of Diffuse Functions in the Structure of $H_3O_2^-$," Carol A. Deakyne, J. Chem. Phys., in preparation.

3. "The Structure of HNO_3^-," Carol A. Deakyne, J. Chem. Phys., in preparation.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The theoretical research conducted under this program was concerned with a study of the structures, total energies, and charge distributions of a series of atmospherically important species. These included OH, OH^-, NH, NH^-, H_2O, NH_2, NH_2^-, OOH, OOH^-, $OH^- \cdot H_2O$, NO_2, NO_2^-, HNO_3, HNO_3^-, and $H_2NO_4^-$. The calculations were carried out ab initio primarily at the MP2/6-31+G** and MP2/4-31+G

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basis set levels. The total energies obtained were used to compute energy changes for several reactions involving the above species and electron affinities for OH, NH, NH_2, OOH, $OH \cdot H_2O$, NO_2, and HNO_3. The theoretical bond lengths, bond angles, electron affinities, and reaction energies are in reasonable agreement with their experimental values, particularly for the MP2/6-31+G** results.

An analysis was performed of the effect of diffuse functions, polarization functions, and electron correlation on the above molecular and thermodynamic properties. It was found that reasonable geometries are obtained without adding diffuse functions to the basis set and reasonable energetics are obtained without adding polarization functions.

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